A Statistical Model Describing Temperature Dependent Gettering of Cu in p-Type Si

Eiji Kamiyama,[a,b,z] Koji Sueoka,[a] and Jan Vanhellemont[c,*]

[a]*Department of Communication Engineering, Okayama Prefectural University, Soja-shi, Okayama-ken 719-1197, Japan*
[b]*GlobalWafers Japan Co., Ltd., Seiro, Niigata, 957-0197, Japan*
[c]*Department of Solid State Sciences, Ghent University, Ghent B-9000, Belgium*

A model is proposed describing quantitatively the temperature dependent gettering of Cu atoms in p-type Si wafers by taking into account the densities and the binding energies of all types of occupying sites, including the gettering ones. Binding energy in this context is defined as the decrease of the formation energy from the reference energy of the Cu atom when it is located at the T-site through which Cu atoms wander through the silicon lattice. By using a statistical approach, the model allows to predict the thermal equilibrium concentration of Cu atoms in each part of a wafer structure. The calculated results show good agreement with reported experimental observations. This model can also be applied to calculate thermal equilibrium concentrations of any contaminant.
 [DOI: 10.1149/2.0131507jss]

Manuscript submitted March 24, 2015; revised manuscript received April 15, 2015. Published April 25, 2015.

Gettering techniques are becoming more important for Si based VLSI manufacturing processes as the device feature size further shrinks.[1] Heavily B doped Si substrates with a low doped epitaxial Si layer are one of the most promising solutions for the multi-chip-module. Their high gettering capacity even when the chip is reduced to a thickness of about 30 μm has been experimentally evaluated by using thinned epitaxial wafers intentionally contaminated with Cu followed by thermal anneals simulating process steps.[2] Meanwhile, Cu is the most important element to develop a gettering technique for as it is widely used for interconnection inside Si device chips and at the same time it can be very harmful when it is present in the junction areas. Cu is also a very fast diffuser in Si and is mobile even at room temperature, see e.g. Ref. 3 and references therein. Among the transition metals, Cu is the only one with a strong segregation at the Si surface after a drive-in from the surface to the bulk of the wafer. This segregation at the surface starts immediately after the surface has been cleaned by hydrochloric acid[4] and occurs even at room temperature during storage of the wafer for a longer time. Due to that, the stability and diffusion behavior of Cu in Si have been investigated extensively on the atomic scale.[5–7] These approaches, however, are limited to the bulk and do not explain the Cu behavior near and at the Si surface.

In the present paper, a statistical method is proposed to describe quantitatively the temperature dependent behavior of Cu atoms in p-type Si on the atomistic scale. In this model, the densities and the binding energies with Cu of all types of gettering sites present in the wafer are taken into account, including also Cu gettering at the Si surface. The application of the model is illustrated with an analysis of Cu gettering by the p^+ or p^{++} substrate in p^- epitaxial wafers as a function of the substrate thickness and the temperature and comparison with results of published gettering experiments.

Theoretical Background and Proposed Model

All gettering techniques are based on atomistic phenomena since the individual metal atoms that are diffusing through metastable sites are captured by stable gettering sites in the wafer. Therefore, a quantitative gettering model should be constructed by using an atomistic approach taking into account the type and total number of each type of gettering site including of course also the decrease of the formation energy, which is defined as the binding energy of a Cu atom to that gettering site. This formation energy decrease happens not only when a Cu atom binds to substitutional B atom but also when a Cu atom with a different charge state is formed by the change of the Fermi level leading to an increased Cu solubility in a heavily doped crystal. Such model has to include also a description of gettering at the wafer surface for which the existence of binding sites for Cu atoms at the Si surface is assumed. In published gettering simulations, however, in most cases the thermal equilibrium concentrations of metals in bulk Si are given as the surface boundary condition.[8]

Building of such an overall gettering model is illustrated for a two-layer Si structure shown schematically in Fig. 1a. The number of sites available for Cu atoms gettering in such two-layer structure depends on the thickness and the doping type and concentration in each layer and of course also on the surface condition. In the present study, the impact of the layer thicknesses and the dopant (in this case, boron) concentration is investigated for the structures listed in Table I. Values of N^i, the number of available gettering sites per square cm, are summarized in Table II. The epitaxial layer and the substrate shown in Fig. 1a are the device layer and the gettering layer, respectively.

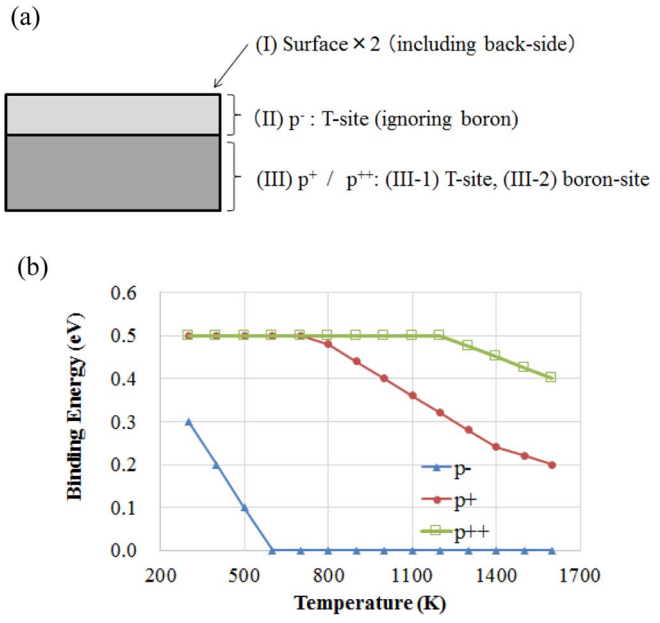

Figure 1. (Color online) (a) Schematic view of the two layer system that is investigated in the present paper, (b) Calculated binding energy of a Cu atom at the T-site as a function of the temperature for three boron concentrations (also see Table I).[9]

*Electrochemical Society Active Member.
[z]E-mail: ejkamiyama@aol.com

Table I. The thickness and boron concentration of each two layer structure used in the present study.

Wafer type	(A)	(B-1)	(B-2)	(B-3)	(B-4)	(B-5)
Epi. (p^-) layer thickness (μm) B: 1×10^{15} cm^{-2}	512	3	3	3	3	3
Sub. thickness (μm) B: 1×10^{19} cm^{-2} for p^+ or 5×10^{19} cm^{-2} for p^{++}	0	750	100	50	30	10

Table II. Site density in each layer per unit area of the wafer surface for the two-layer structures of Table I.

Candidate site density N^i for gettering Cu atoms (cm^{-2})		(A)	(B-1)	(B-2)	(B-3)	(B-4)
(I) Surface (both sides)		2.7×10^{15} (see in the text)				
(II) p^-	T-site	2.6×10^{21}	1.5×10^{19}			
(III) p^+/p^{++}	T-site	0	3.8×10^{21}	5.0×10^{20}	2.5×10^{20}	1.5×10^{20}
	Boron-site	0	7.5×10^{17}/ 3.8×10^{18}	1.0×10^{17}/ 5.0×10^{17}	5.0×10^{16}/ 2.5×10^{17}	1.0×10^{16}/ 5.0×10^{16}

Table III. Comparison between fitted results using the present model and experimental data in literature.

	Fitting parameter	Fitted results using this model		Experimental data [4]		
Contamination level (cm^{-2})	Binding energy at surface site (eV)	Surface (cm^{-2}; one side)	Bulk (cm^{-3})	Front surface (cm^{-2})	Back surface (cm^{-2})	Bulk (cm^{-3})
[L] 2.2×10^{11}	1.387	2.4×10^{10}	1.9×10^{12}	2.4×10^{10}	2.4×10^{10}	-
	1.231	7.8×10^{09}	3.0×10^{12}			
[M] 2.2×10^{12}		7.8×10^{10}	3.0×10^{13}	2.0×10^{11}	1.8×10^{11}	-
[H] 2.2×10^{13}		7.8×10^{11}	3.0×10^{14}	7.8×10^{11}	7.8×10^{11}	3.2×10^{14}

Assuming that the total numbers of B and Cu atoms are constant in the considered two layer structure, one can calculate the thermal equilibrium values statistically by introducing the partition function Z. Ignoring in first order approximation the entropy contribution of phonons to the enthalpy, Z can be written in the standard form used in thermal-statistics as

$$Z = \sum_i N^i \exp\left[-\frac{E_b^i}{k_B T}\right] \quad [1]$$

$E_b{}^i$ is the binding energy of a Cu atom with the i-type gettering site, k_B is the Boltzmann's constant and T is the absolute temperature. In this equation, the energy of the Cu atom at the tetrahedral (T) site of the layer containing the lowest boron concentration is used as reference. At the gettering temperature the Fermi level in that layer is located close to mid gap. Fermi level effects on the charge state of Cu at the T-site are taken into account by using the calculated binding energy[9] as function of the Fermi level determined by boron concentration and temperature. The results are shown in Fig. 1b. The probability p^i of the presence of a Cu atom at an i-type gettering site, can be written as

$$p^i = \left\{N^i \exp\left[-\frac{E_b^i}{k_B T}\right]\right\} \Big/ Z. \quad [2]$$

Knowing the total contamination concentration, it is straightforward estimating the expected thermal equilibrium Cu concentrations in each layer using p^i at the given temperature.

Comparison with Published Experimental Data

Cu atoms segregate at the Si surface due to a lower formation energy by interaction with the surface. The amount of this lowering of the formation energy has not been investigated theoretically by using ab initio calculations and also not experimentally. Using the present model, this energy can be estimated by fitting to e.g. the experimental data obtained by Shabani et al.[4] In that study, 125 mm diameter wafers were used with a thickness of about 0.64 mm and a boron doping of about 1.3×10^{15} cm^{-3}. In the present study, the site density for binding Cu atoms at a Si(100) wafer surface is assumed to be equal to the density of the dangling bonds at that Si which is about 2.7×10^{15} cm^{-2}. This is a good assumption when the gettering sites exist in a mono-layer near the surface similar to self-interstitials at T like site positions near the Si (100) surface found by ab initio calculation.[10] The present paper also considers only low contamination levels whereby no copper silicide phase is formed and copper atoms can move inside the wafers reversibly as Shabani et al. discussed.[4] With these assumptions, it is straightforward to reproduce the experimental results of Shabani et al. within the experimental error, assuming that the binding energy for Cu atoms at a Si surface is 1.231 eV for the highest level of Cu contamination labeled as [H] in Table III.[4] For lower Cu contamination levels,[4] however, this binding energy value leads to significant deviations as shown for the [M] and [L] cases in Table III. This is probably due to the delay of diffusion to the surface caused by the band bending[8] or the repulsive Coulomb interactions between antecedently out-diffused Cu atoms and followingly diffusing Cu atoms to the surface, both of which have positive charges in p-type Si. Therefore, the binding energy obtained for the lowest level one of contamination is probably the most reliable estimate of the binding energy of Cu atoms at a wafer surface. Thus, the binding energies used in the present study for the analysis of the distribution of Cu atoms in two-layer Si structures are summarized in Table IV and Fig. 1b. The binding energy of the Cu-B pair is reported to be 0.57 eV.[6]

Table IV. Binding energies E_b, which are applied for the calculation of the distribution of copper atoms in a wafer, using Eq. 1 and Eq. 2.

	Eb (eV)
T-site	See Fig. 1b
Surface	1.387
Boron-site	0.57

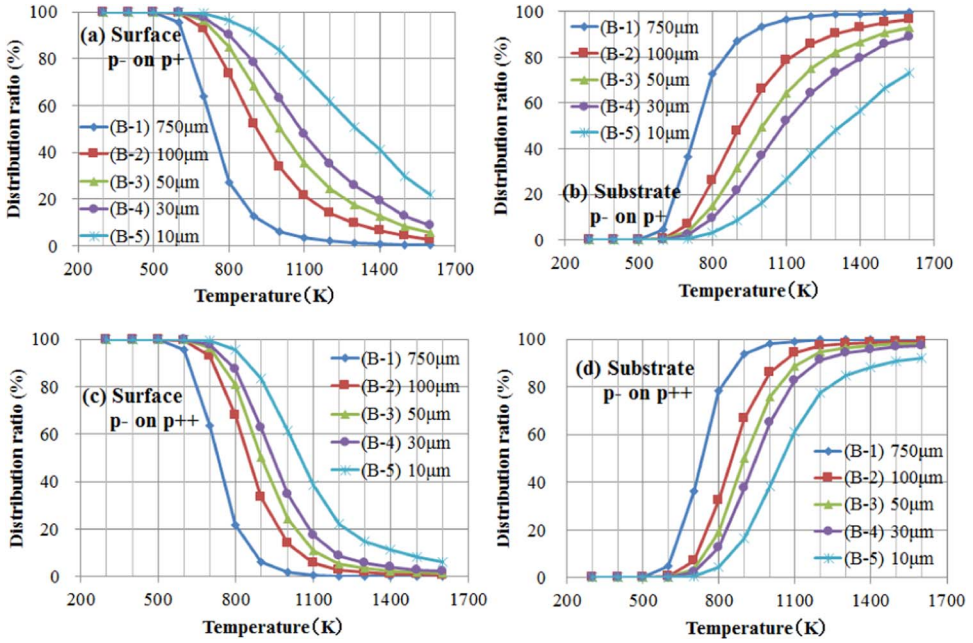

Figure 2. (Color online) Calculated distribution ratios as function of the temperature of Cu atoms of (a) surface of a p^+ substrate, (b) the p^+ substrate itself, (c) surface of a p^{++} substrate and (d) the p^{++} substrate itself. Both the p^+ and p^{++} substrates are covered with a 3 μm epitaxial p-layer.

By using Eq. 1 and Eq. 2, the distribution ratios of Cu atoms between surface and substrate for the heavy doped layer thickness range between 750 μm and 10 μm (from B-1 to B-5 in Table I) and a 3 μm epitaxial p^- layer on a p^+ or p^{++} substrate, respectively, are calculated as function of the temperature. The results for surface and five substrate thicknesses are shown in Fig. 2a and 2b for p^+ substrate and in Fig. 2c and 2d for p^{++} substrate, respectively. At room temperature, Cu atoms are gettered at the surface for both wafers, due to the high Cu binding energy at the wafer surfaces in agreement also with the observed out-diffusion of Cu to wafer surfaces at room temperature[3] due to the fact that below 600 K, the surface is simply the strongest getterer (Fig. 2). As the temperature increases, Cu atoms tend to move more into the substrate, due to the high density of T-sites in bulk Si. This trend is enhanced due to the Fermi level effect in the heavy doped layer with increasing B concentration.

The calculated dependence of the gettering efficiency on the temperature and on the substrate thickness is shown in Fig. 3a for a p^+ substrate and in 3(b) for a p^{++} substrate, respectively. The gettering efficiency is 0%, when no contamination is detected in the substrate, and is 100% when all the Cu contamination introduced on the wafer surface before the gettering step is detected in the substrate after the gettering treatment. The open circle, triangle and square are based on published experimental data.[2] These points are obtained by converting the value in literature for the concentration detected on a single surface by taking into account that Cu gettering occurs at both surfaces of the wafer. These open symbols are plotted at the maximum temperature in the anneal recipe used in the experiment. The good agreement with the calculated curves suggests that Cu out-diffusion to the surface is slow, as was also observed in Shabani's experiments.[4]

Discussion

The described statistical model is able to predict the temperature dependent gettering of Cu atoms in any type of wafer structure if the gettering site density and the corresponding binding energy are known. The model also has the advantage that gettering phenomena can be calculated based on ab initio calculation results. Ab initio calculations indeed allow calculating the binding energy of any kind of contamination atom at any position in crystals using the same approach as in the present model without the need to perform experiments. The model does however not include nonequilibrium phenomena such as nucleation of other phases, e.g., silicides inside the wafer or at the surface. Diffusion effects can in principle be included into the

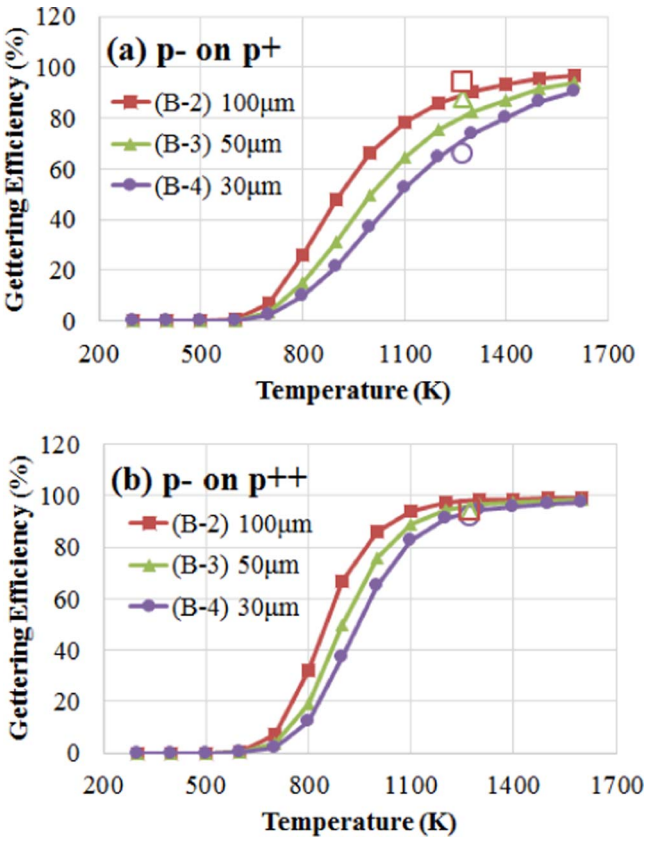

Figure 3. (Color online) Calculated dependence of gettering efficiency on the temperature for a 3 μm epitaxial wafer with (a) p^+ substrate and (b) p^{++} substrate, respectively of 100, 50 and 30 μm thickness Open circle, triangle and square symbols are published experimental data.[2]

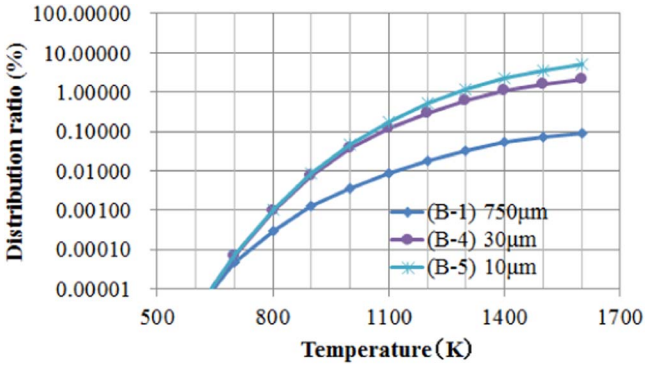

Figure 4. (Color online) Distributions ratio of Cu atoms between a moderately B doped epitaxial layer (p^- device layer) and a heavily B doped substrate layer (p^+ substrate) with thickness of 750, 30 and 10 μm layer, calculated as function of the temperature.

model by taking into account the spatial distribution of T sites and the diffusivity of impurity atoms. This is under study and results will be published elsewhere. Within the current stage of this model, one can predict the expected behavior as function of temperature by considering the change of thermal equilibrium probabilities.

In the past, there was a dispute between experimentalists about the type of gettering for Fe in Si wafers with poly back seal, i.e., relaxation-induced gettering[11,12] or segregation-induced gettering.[13,14] Relaxation-induced gettering was considered to occur when the concentration of metal atoms exceeded the thermal equilibrium concentration. In other words, metal supersaturation is the driving force in that case. Segregation-induced gettering was considered to occur when a non-uniformity exists in the wafer of the ratio between the actual and the thermal equilibrium concentration. In this case, the driving force for gettering is the difference of chemical potentials. The proposed model, however, can treat these two types of gettering by only considering the number of gettering sites and their binding energies by taking into account also the Fermi level dependence. When the gettering capability of the substrate layer is increased due to a larger number of gettering sites and/or a larger binding energy than in the device layer, the thermal equilibrium concentration of Cu atoms in the device layer is lowered as shown for sample (B-1) in Fig. 4. In this case, it will meet the criteria of the so called "relaxation-induced gettering". When these differences between device layer and substrate layer decrease e.g. with decreasing substrate layer thickness, however, the chemical potentials and number of gettering sites become nearly equal as shown for sample (B-4) in Fig. 4. Fig. 4 shows clearly the dependence on p^+ substrate thickness of the gettering capacity although very good gettering performance is still obtained for a 30 μm thin p^+ substrate for anneal temperatures below 800°C in agreement with the results of An et al.[2] The figure also suggests that it is even feasible to use a 10 μm p^+ layer, assuming that the appropriate processing temperature is chosen. In addition, once a new type of gettering site, such as a silicide precipitate, is created inside the wafer or at the wafer surface, the partition function will be totally changed. To take into account also gettering by complicated structures such as silicide or silicon oxide precipitates,[15] in the present model is planned for the near future.

Conclusions

A statistical model for describing the gettering of impurities on the atomistic scale is proposed and illustrated for the gettering of Cu atoms in a p-type Si double layer structure consisting of a moderately B doped layer, the "device layer", and a heavily B doped layer, the "substrate". This statistical model can predict the thermal equilibrium concentrations and the distribution of metallic contamination atoms in advanced wafer structures if the gettering site densities and their binding energies for the metallic impurity atoms are known.

References

1. H. Tsuya, *Jpn. J. Appl. Phys.*, **43**, 4055 (2004).
2. J. H. An, J. S. Kim, J. Y. Kim, K. S. Lee, H. B. Kang, B. S. Moon, S. H. Lee, Y. Shin, S. M. Hwang, and H. Y. Park, *ECS Transactions*, **50**, 319 (2012).
3. D. Kot, G. Kissinger, A. Sattler, and T. Műller, *Acta Physica Polonica A*, **125**, 965 (2014).
4. M. B. Shabani, T. Yoshimi, and H. Abe, *J. Electrochem. Soc.*, **143**, 2025 (1996).
5. K. Shirai, T. Michikita, and H. Katayama-Yoshida, *Jpn. J. Appl. Phys.*, **44**, 7760 (2005).
6. T. Michikita, K. Shirai, and H. Katayama-Yoshida, *Jpn. J. Appl. Phys.*, **44**, 7904 (2005).
7. K. Matsukawa, K. Shirai, H. Yamaguchi, and H. Katayama-Yoshida, *Physica B*, **401**, 151 (2007).
8. A. A. Istratov and E. R. Weber, *J. Electrochem. Soc.*, **149**, G21 (2002).
9. H. Yamaguchi, K. Shirai, and H. Katayama-Yoshida, *J. Comput. And Theoret. Nanoscience*, **6**, 2619 (2009).
10. E. Kamiyama, K. Sueoka, and J. Vanhellemont, *J. Appl. Phys.*, **111**, 083507 (2012).
11. M. B. Shabani, T. Yoshimi, S. Okuuchi, and H. Abe, *Solid State Phenomena*, **57**, 81 (1997).
12. M. B. Shabani, Y. Shiina, and Y. Shimanuki, *The Electrochem. Soc. Proceedings Volume 2000-17*, p. 305, The Electrochem. Soc. Pennington, NJ (2000).
13. S. Ogushi, S. Sadamitsu, K. Marsden, Y. Koike, and M. Sano, *Jpn. J. Appl. Phys.* **36**, 6601 (1997).
14. Y. Hayamizu, S. Tobe, H. Takeno, Y. Kitagawara, and Y. Computer *Simulation of Impurity Gettering Capability in Silicon for Current Gettering Techniques, The Electrochem. Soc. Proceedings Volume 98-1*, p. 1080, The Electrochem. Soc. Pennington, NJ (1998).
15. D. Kot, G. Kissinger, M. A. Schubert, A. Sattler, and T. Müller, *Solid State Phenomena*, **205–206**, 278 (2014).